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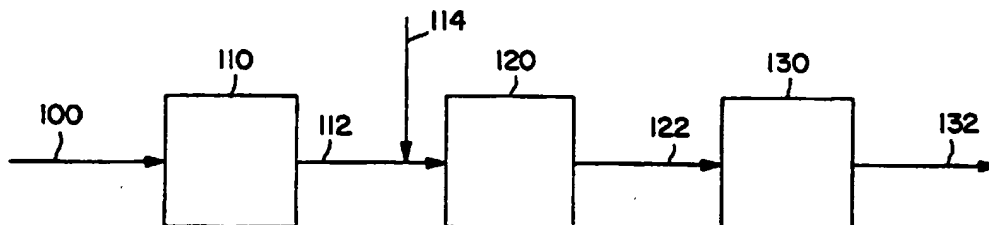
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 COMBUSTION OF HYDROGEN



(57) Abstract

A process for the net catalytic oxidative dehydrogenation of alkanes to produce alkenes is provided. The process involves simultaneous equilibrium dehydrogenation of alkanes to alkenes and combustion of the hydrogen formed to drive the equilibrium dehydrogenation reaction further to the product alkenes. In the present reaction, the alkane feed is dehydrogenated over an equilibrium dehydrogenation catalyst in a first reactor (110) and the effluent, along with oxygen is then passed into the second reactor (120) containing a metal oxide catalyst which serves to selectively catalyze the combustion of hydrogen. The equilibrium dehydrogenation catalyst may comprise platinum and the selective metal oxide combustion catalyst may contain bismuth, antimony, indium, or molybdenum, or a mixture thereof.

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**PROCESS FOR THE CATALYTIC DEHYDROGENATION OF ALKANES
TO ALKENES WITH SIMULTANEOUS COMBUSTION OF HYDROGEN**

This invention relates to a process for the net catalytic oxidative dehydrogenation of alkanes to produce alkenes. The process involves simultaneous equilibrium
5 dehydrogenation of alkanes to alkenes and combustion of the hydrogen formed to drive the equilibrium dehydrogenation reaction further to the product alkenes.

Developments in zeolite catalysts and hydrocarbon
10 conversion processes have created interest in utilizing light aliphatic feedstocks for producing C_5+ gasoline, diesel fuel, etc. In addition to chemical reactions promoted by medium-pore zeolite catalysts, a number of discoveries have contributed to the development of new
15 industrial processes. These are safe, environmentally acceptable processes for utilizing aliphatic feedstocks. Conversions of C_2-C_4 alkenes and alkanes to produce aromatics-rich liquid hydrocarbon products were found by Cattanaach (U.S. Patent No. 3,760,024) and Yan et al. (U.S.
20 Patent No. 3,845,150) to be effective processes using the zeolite catalysts. In U.S. Patent Nos. 3,960,978 and 4,021,502, Plank, Rosinski and Givens disclose conversion of C_2-C_5 olefins, alone or in admixture with paraffinic components, into higher hydrocarbons over crystalline
25 zeolites having controlled acidity. Garwood et al. have also contributed to the understanding of catalytic olefin upgrading techniques and improved processes as in U.S. Patent Nos. 4,150,062; 4,211,640; and 4,227,992. The above-identified disclosures are incorporated herein by
30 reference.

Catalytic dehydrogenation and aromatization of light paraffinic streams, e.g., C_2-C_4 paraffins, commonly referred to as LPG, is strongly endothermic and typically carried out at temperatures between 540° and 820°C (1000°
35 and 1500°F), the problem of transferring sufficient heat to a catalytic reaction zone to carry out the paraffin

upgrading reaction remains as an obstacle to commercialization of these processes.

Dehydrogenation of paraffins to olefins has recently generated increasing interest as the market value of olefinic intermediate feedstocks continues to rise. Light olefins, particularly C_2 - C_4 olefins, enjoy strong demand as building blocks for a wide range of valuable end products including fuels and specialized lubricants as well as thermoplastics.

Methods for supplying heat to an endothermic reaction zone include indirect heat exchange as well as direct heat exchange. Indirect heat exchange is exemplified by a multi-bed reactor with inter-bed heating or a fluid bed reactor with heat exchange coils positioned within the catalyst bed. Direct heat exchange techniques include circulation of inert or catalytically active particles from a high temperature heat source to the reaction zone, or the coupling of a secondary exothermic reaction with the primary endothermic reaction in a single catalytic reaction zone. Examples of such secondary exothermic reactions include (1) oxidative dehydrogenation of a portion of the feedstream, (2) sacrificial co-combustion of a part of the alkane/alkene mixture, and (3) combustion of carbonized species (e.g., coke) on the catalyst.

Currently known techniques for oxidative dehydrogenation are unfortunately not selective enough to achieve sufficiently high levels to allow for commercial practice and at least a part of the valuable product is over-oxidized, usually to the waste products, CO , CO_2 , and H_2O .

Examples of such sacrificial co-combustion processes include those described in U.S. Patent No. 3,136,713 to Miale et al. which teaches a method for heating a reaction zone by selectively burning a portion of a combustible feedstream in a reaction zone. Heat is directly transferred from the exothermic oxidation reaction to

supply the endothermic heat for the desired conversion reaction.

A process for the oxidative dehydrogenation of propane is described in U.S. Patent No. 5,086,032 to Mazzocchia et al.

Heat balanced reactions are also taught in U.S. Patent Nos. 3,254,023 and 3,267,023 to Miale et al. Additionally, U.S. Patent No. 3,845,150 to Yan and Zahner teaches a heat balanced process for the aromatization of hydrocarbon streams by combining the exothermic aromatization of light olefins with the endothermic aromatization of saturated hydrocarbons in the presence of a medium-pore zeolite catalyst.

Turning now to chemical reaction thermodynamics, it is well recognized that the extent of reaction may be increased by removing reaction products from contact with the reactants as the reaction products are formed. This principle finds application in U.S. Patent No. 3,450,500 to Setzer et al. which teaches a process for reforming hydrocarbon feedstocks and withdrawing the hydrogen product from contact with the feedstock driving the equilibrium to favor increased hydrogen production. Articles by Shu et al. and by Ziaka et al. teach that the extent of reaction for equilibrium dehydrogenation reactions may be further driven to product olefin by the concomitant removal of the hydrogen formed with hydrogen selective membranes. The article by Shu et al. appears in the Canadian Journal of Chemical Engineering, 69, 1036-1060 (1991); and the article by Ziaka et al. entitled "A High Temperature Catalytic Membrane Reactor for Propane Dehydrogenation" appears in the Journal of Membrane Science, 77, 221-232 (1993).

Similarly, British Patent Application GB 2190397A describes a process for producing aromatic hydrocarbons by catalytic paraffin dehydrocyclodimerization. The process upgrades C_2 - C_6 paraffins, i.e., ethane, propane, butane or a mixture thereof to a mixture of aromatic hydrocarbons and

hydrogen by-product in a reactor provided with a membrane capable of selective, in-situ transfer of at least a portion of the hydrogen in the mixture across the membrane. Catalysts useful in the paraffin upgrading process are said to include zeolites, and in particular gallium-containing zeolites.

It is believed that the paraffin dehydrogenation reaction is equilibrium limited when carried out in a conventional reactor due to the thermodynamics of equilibrium dehydrogenation. For example, at 550°C the equilibrium propylene from propane dehydrogenation, irrespective of catalyst, is limited to 33%. Thus, the state of the art of endothermic hydrogen-producing paraffin upgrading processes would clearly be advanced by a process and apparatus for increasing the extent of reaction while also providing a high temperature heat source to supply at least a portion of the endothermic heat of reaction.

The present invention provides a process for converting an alkane of the formula,

$$C_n H_{2n+2},$$
to an alkene of the formula,

$$C_n H_{2n},$$
where n is the same for the alkane and the alkene and n is from 2 to 5, the process comprising the steps of:

- (a) contacting the alkane with a solid material comprising a dehydrogenation catalyst under conditions sufficient to produce the alkene and H_2 , wherein the dehydrogenation catalyst comprises at least one metal selected from Cr, Mo, Ga, Zn and a Group VIII metal;
- (b) contacting the effluent from step (a) with an oxidation catalyst and oxygen under conditions sufficient to selectively convert the H_2 to water, wherein the oxidation catalyst comprises an oxide of at least one metal selected from Bi, In, Sb, Zn, Tl, Pb and Te; and
- (c) contacting at least a portion of the effluent of step (b) with a solid material comprising a dehydrogenation

catalyst under conditions sufficient to convert unreacted alkane to additional quantities of the alkane and H_2 .

Figure 1 provides a schematic diagram of an example of the present process, wherein a first dehydrogenation reactor is connected in series to an oxidation reactor which is, in turn, connected to a second dehydrogenation reactor.

Figure 2 provides a schematic diagram of an example of the present process, wherein a dehydrogenation reactor is connected to an oxidation reactor in a manner which facilitates recycle of the effluent from the oxidation reactor back into the dehydrogenation reactor.

Figure 3 is a graph showing conversion of H_2 and propylene over Bi_2O_3/SiO_2 during the course of 120 REDOX cycles.

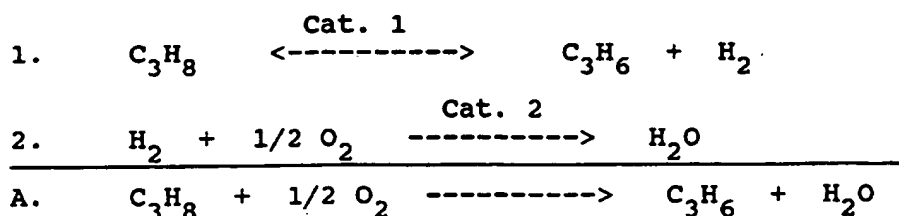
Figure 4 is a graph showing conversions of hydrogen and propane as a function of residence time in a reactor.

Figure 5 is a graph showing conversions of hydrogen and propylene as a function of residence time in a reactor.

20 Embodiments

Alkanes are converted to olefins (and dienes) by an integrated process scheme which involves the direct equilibrium dehydrogenation of alkanes via known catalysts and the selective oxidation of the resulting hydrogen gas thus formed. The light paraffins which may be utilized for such reactions include C_2 - C_5 , such as propane and isobutane. As an illustrative example, the overall reaction scheme, demonstrated for propane conversion to propylene, is thus:

30 Scheme A:



Reaction 1 is documented in the literature and is known as propane equilibrium dehydrogenation. Butane and isobutane equilibrium dehydrogenation are also known and documented in the literature. Reaction 1 has been demonstrated to occur catalytically over $\text{Cr/Al}_2\text{O}_3$, $\text{Mo/Al}_2\text{O}_3$, iron-based catalysts, supported (supports include silica, alumina, zirconia, titania, and thoria) and unsupported noble metals (e.g., Pt, Pd, Rh, Ir, Ru, etc), and supported and unsupported gallium and zinc oxides. Reaction 2 can proceed in the absence (redox mode), as opposed to the presence (cofed mode) of gaseous oxygen, over a number of reducible metal oxides. Catalyst 1 and Catalyst 2 may be used together or in separate reactors.

Several recent, open literature reports have discussed the oxidative dehydrogenation of propane and butane to the corresponding olefins. These reactions are typically carried out by utilizing a mixture of alkane and oxygen cofed over a metal oxide catalyst. Typical operating temperatures are from 400 to 600°C, 101 to 505 kPa (1 to 5 atm) pressure, either with a diluent or in the absence of one.

The present invention differs from the system described above in that the reaction involves two separately functioning catalysts--an equilibrium dehydrogenation catalyst, and a hydrogen combustion catalyst. These components may be used in separate reactors, connected in series or in a recycle mode, so as to drive the equilibration reaction (equation 1 above) further to the product side than is normally possible with only an equilibration catalyst. Thus, in the present scheme, the hydrogen would be combusted to H_2O (or at least a portion of it), thus driving the equilibrium represented by equation 1 to the side of the products.

The catalyst used in the dehydrogenation reaction may be an equilibrium dehydrogenation catalyst comprising a Group VIII metal (i.e., Fe, Co, Ni, Ru, Rh, Pd, Os, Ir or

Pt). Of these Group VIII metals, the noble metals (i.e., Ru, Rh, Pd, Os, Ir) are preferred. These Group VIII metals are preferably present in an at least partially reduced state with at least a portion thereof being in the free metal (i.e., zero valent) form. Examples of such equilibrium dehydrogenation catalysts include (1) Pt, Pd or other Group VIII metals either in bulk phase or supported on oxide supports (alumina, silica, titania, zirconia, zinc aluminate, etc.).

10 A particular dehydrogenation catalyst, which may be used in the present dehydrogenation reaction is a Pt/Sn/ZSM-5 catalyst, especially as described in U.S. Patent Nos. 4,990,710 and 5,192,728. Such Pt/Sn/ZSM-5 catalysts may comprise 0.1 to 20 weight percent platinum and 0.1 to 20 weight percent tin with the remainder being ZSM-5. The ZSM-5 in this catalyst is essentially non-acidic and may comprise less than 0.1 weight percent of aluminum.

20 By means of the present invention, whereby hydrogen is selectively oxidized after being produced in the dehydrogenation of an alkane, it is possible to obtain greater than equilibrium yields of alkenes from the overall process. The following table provides thermodynamic calculations of equilibrium yields of propylene, butene, and isobutene from propane, n-butane, and i-butane, respectively.

	<u>Temperature, °C</u>	<u>Propane</u>	<u>n-Butane</u>	<u>i-Butane</u>
	350	2	3	4
	400	4	7	8
30	450	9	15	18
	500	18	28	33
	550	32	46	53
	600	50	66	72
	650	68	82	85
35	700	82	92	93

Figure 1 provides a schematic diagram of an example of the present process, wherein a first dehydrogenation reactor is connected in series to an oxidation reactor which is, in turn, connected to a second dehydrogenation reactor. In Figure 1, a suitable alkane feed, such as propane, is introduced into dehydrogenation reactor 110 via line 100. The effluent from reactor 110, comprising alkene, hydrogen and unreacted alkane, passes through line 112 to oxidation reactor 120, wherein hydrogen is selectively oxidized. Oxygen, e.g., air, may be introduced into reactor 120 via lines 114 and 112. The effluent from the oxidation reactor, comprising unreacted alkane, alkene and a reduced amount of hydrogen, then passes through a second dehydrogenation reactor 130, wherein unreacted alkane from the first dehydrogenation reactor is converted to additional alkene and hydrogen. The product from reactor 130 may be recovered via line 132 or it may be passed via line 132 to one or more oxidation reactors, each followed by a dehydrogenation reactor connected in series.

Figure 2 provides a schematic diagram of an example of the present process, wherein a dehydrogenation reactor is connected to an oxidation reactor in a manner which facilitates recycle of the effluent from the oxidation reactor back into the dehydrogenation reactor. In Figure 2, a suitable alkane feed, such as propane, is introduced into dehydrogenation reactor 210 via line 200. The effluent from reactor 210, comprising alkene, hydrogen and unreacted alkane, passes through line 212 to oxidation reactor 220, wherein hydrogen is selectively oxidized. Oxygen may be introduced into reactor 220 via line 214. The effluent from the oxidation reactor, comprising unreacted alkane, alkene and a reduced amount of hydrogen, then passes through recycle line 222 to line 200 and back into dehydrogenation reactor 210, wherein unreacted alkane from the first dehydrogenation reactor pass is converted to additional alkene and hydrogen. The number of passes or

recycle steps through the system depends on the desired level of alkane conversion to alkene product. When a sufficient level of conversion is achieved, the product may be recovered via line 232 or it may be passed via line 232 to a series of one or more additional oxidation and dehydrogenation reactors.

The recycle reaction scheme shown in Figure 2 may be operated in a batch or continuous mode. In the batch mode, the flow of fresh alkane feed to reactor 210 via line 200 is shut off at a certain point in time so that the recycle stream from line 222 becomes the only source of reactant in reactor 210. While this batch mode recycle reaction is taking place, line 232 remains closed. After a desired level of conversion is achieved, line 232 may be opened and product recovered. The introduction of a flush gas, such as nitrogen, into the system, e.g., via line 214, may facilitate recovery of the product.

In a continuous mode, line 232 may be partially opened so that a metered amount of product is withdrawn, while the remainder of the effluent from reactor 210 passes into the oxidation reactor 220 via line 212. As a portion of the product is being continuously withdrawn via line 232, a corresponding amount of fresh alkane feed is introduced into reactor 210 along with the recycle stream.

As described in the Examples below, particularly selective combustion of hydrogen over alkanes or alkenes is not a property common to all metal oxides but rather is limited over a fairly narrow selection of metal oxides found to possess this particularly selective hydrogen combustion capability.

As is shown in Examples below, the oxides of bismuth are particularly selective for hydrogen combustion over hydrocarbon combustion, while the oxides of vanadium are not.

The metal oxides, which are particularly selective for the present selective hydrogen combustion reaction, contain certain metals selected from a narrow quadrant of the periodic table, i.e., the upper right hand corner thereof.

5 These metals include Bi, In, Sb, Zn, Tl, Pb and Te. A review of the periodic table suggests that this group of elements is centered by the location of the particular elements, Bi, In and Sb.

In addition to the catalytic metal oxide, the
10 oxidation catalyst may include other components such as supports for the catalytic metal oxide. Examples of such supports include nonreducible, essentially inert oxides, such as silica, alumina, zirconia, titania, hafnia, and mixtures of these oxides, such as silica/alumina. Other
15 optional components of the present oxidation catalyst include certain elements, particularly in oxide form, which have been used as promoters for known oxidation or oxidative dehydrogenation catalysts. Particular examples of oxides, which may be optionally included in the present
20 oxidation catalyst, include one or more oxides of elements selected from the group consisting of Mo, W, P and La. Although the question of whether such oxides of Mo, W, P and La actually have a beneficial or promoting effect in the present selective hydrogen combustion reaction has been
25 largely unexplored, it is at least believed that these particular oxides do not have a detrimental effect.

Although oxides of Mo, W, P and La, as well as oxides of Si, Al, Zr, Ti and Hf, need not be avoided in the present oxidation catalyst, other oxides, which tend to
30 promote the oxidation of alkanes and alkenes, should be avoided. Examples of such oxides, which are preferably not included in the present oxidation catalyst, includes oxides of one or more of the following elements: V, Fe, Cu, Nb and Ta.

The oxidation catalyst may contain, for example, at least 1 weight percent of catalytically active metal oxide. Elemental analysis of the oxidation catalyst may reveal the presence of, for example, at least 0.5 weight percent of one or a combination of metals selected from the group consisting of Bi, In, Sb, Zn, Tl, Pb and Te.

The oxidation catalyst described herein may be an oxide of a single metal, such as bismuth or antimony, or it may be a mixed metal oxide. An example of a mixed metal oxide is a compound of the following empirical formula



where

- A = P, La, Ce, Y, Ru, Co, Ni, Cu, Al, In, Ga, and/or Ge
B = Mo, W, Cr, Sn, Nb, Ta, and/or Ti
C = an alkali, an alkaline earth, Ag, and/or Tl
O = oxygen

where

- a, b, c = 0 to 12
a + b + c > 0
d = 0 to 12
e = 0 to 12
f = 0 to 12
x = dictated by the oxidation states of the remaining elements.

Another example of a mixed metal oxide is a compound of the following empirical formula



where

- A = In, Cr, Al, Zn, Pb, and/or a Rare Earth (preferred RE = Tb, Gd, Ce, Y, and/or La)
B = La, Ce, Y, Ru, Fe, Co, Ni, Cu, Al, In, Ga, and/or Ge
C = P, Mo, W, Cr, Sn, Nb, Ta, and/or Ti
D = an alkali, an alkaline earth, Ag, and/or Tl
O = oxygen

where

$$0 < a < 12$$

$$b = 0 \text{ to } 12$$

$$c = 0 \text{ to } 12$$

5 $d = 0 \text{ to } 12$

$$e = 0 \text{ to } 12$$

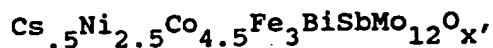
$x =$ dictated by the oxidation states of the remaining elements.

EXAMPLE 1

10 In this Example, it is demonstrated that some metal oxides can be reduced much faster by hydrogen than by hydrocarbons; hence, they exhibit superior selective hydrogen combustion (SHC) properties.

15 A gravimetric, Cahn balance apparatus was used to measure the reduction rates of several metal oxides with hydrogen and C_3 hydrocarbons at 500°C . These rates and the selectivity of the examined oxides for SHC are listed in Table 1.

20 In Table 1, MCC (multicomponent catalyst) stands for a compound of the formula



where x is dictated by the oxidation states of the remaining elements. Also in Table 1, $[O]_L$ stands for lattice oxygen.

Table 1

Selectivities of SHC Catalysts at 500°C for the Removal of
Lattice Oxygen to Convert Hydrogen vs. Propane,
Measured by Gravimetry

5	Metal Oxide	Wt.% [O] _L Removed By:		Hydrogen to form water ^a	Propane to form propylene, CO _x , and water ^b
		Hydrogen	Propane		
10	Bi ₂ Mo ₃ O ₁₂	10.2	0.10	99.0	1.0
	In ₂ Mo ₃ O ₁₂	12.9	0.21	98.4	1.6
	Al ₂ Mo ₃ O ₁₂	5.36	0.25	95.5	4.5
	Bi ₂ O ₃	8.85	0.44	95.3	4.7
	Fe ₂ Mo ₃ O ₁₂	3.32	0.21	94.0	6.0
15	MCC	8.6	0.95	90.1	9.9
	Cr ₂ Mo ₃ O ₁₂	6.97	0.91	88.5	11.5
	La ₂ Mo ₃ O ₁₂	1.02	0.17	85.7	14.3
	Ce ₂ Mo ₃ O ₁₂	1.04	0.27	79.4	20.6
	MoO ₃	1.0	0.28	78.1	21.9
20	V ₂ O ₅	0.9	13.6	6.2	93.8

^a % selectivity for H₂ =
wt.%[O]_L removed by H₂

25 wt.% [O]_L removed by H₂ + wt.%[O]_L removed by C₃[•]
^b % selectivity for C₃[•] =
wt.%[O]_L removed by C₃[•]

wt.% [O]_L removed by C₃[•] + wt.%[O]_L removed by H₂

30 Table 1 shows that Bi₂O₃; indium, bismuth, lanthanum,
cerium, and aluminum molybdates; and MCC exhibit the
highest selectivities for hydrogen combustion in the
presence of propane, while V₂O₅ exhibits the lowest.

EXAMPLE 2

An equimolar mixture of 15% hydrogen and 15% propylene in helium was passed over 1 g of 42% Bi_2O_3 /58% SiO_2 at a total flowrate of 170 cc/min at 550°C for 140 seconds. The product gas was collected and analyzed with gas chromatography. H_2 conversion to H_2O was greater than 85%, while the conversion of propylene was less than 0.5%.

EXAMPLE 3

The same experiment was conducted as in Example 2, except that the feed was flowed over the sample for 600 seconds at a total flowrate of 40 cc/min. The H_2 conversion in the reactor effluent was 79%, while the conversion of propylene was approximately 1%.

EXAMPLE 4

An equimolar mixture of 15% hydrogen and 15% propane in helium was passed over 1 g of 50% V_2O_5 /50% Al_2O_3 at a total flowrate of 170 cc/min at 550°C for 140 seconds. The product gas was collected and analyzed with gas chromatography. H_2 conversion to H_2O was 81%, while the conversion of propane, mostly to CO , CO_2 , and H_2O , was 23%.

EXAMPLE 5

The same experiment was conducted as in Example 4, except that the feed was flowed over the sample for 600 seconds at a total flowrate of 40 cc/min. The H_2 conversion in the reactor effluent was only 11%, while the conversion of propane to waste products was 24%. Examples 4 and 5 illustrate that, in sharp contrast to Bi_2O_3 , V_2O_5 does not exhibit SHC properties, since its lattice oxygen is particularly active for the conversion of hydrocarbons.

EXAMPLE 6

The same material as in Examples 2 and 3 was exposed to 120 consecutive redox cycles. A redox cycle consists of an oxidation phase (flow of excess air for 5 minutes) followed by a reduction phase (flow of 15% H_2 , 15% $C_3^=$ at 170 cc/min for 140 seconds). The oxidation and reduction phases are separated by two helium purge phases. The H_2 conversion as a function of cycle number is shown in Figure 3. The conversion of propylene was negligibly small (less than 0.5%), mostly to CO_2 . The conversion of H_2 is attributed to its oxidation to H_2O by the lattice oxygen of Bi_2O_3 which did not oxidize virtually any of the hydrocarbon present.

EXAMPLE 7

In this Example, it is demonstrated that Bi_2O_3 is selective for combustion of H_2 in the presence of hydrocarbons and also in the presence of cofed gaseous oxygen.

The activity and selectivity of Bi_2O_3 in the cofed mode was examined using equimolar $H_2-C_3^=$ and $H_2-C_3^=$ mixtures, with stoichiometric amounts of gaseous oxygen (15% $C_3^=$, 15% H_2 , 7.5% O_2). Shown in Figure 4 are the conversions of hydrogen and propane at 500°C as a function of residence time. The propane conversion, mostly to CO_2 , was always less than 2%, while the conversion of hydrogen exceeded 90% at high residence time. This indicates that the deliberately limited supply of cofed oxygen had been utilized very selectively to preferentially activate the hydrogen gas.

Shown in Figure 5 are the corresponding results with a hydrogen/propylene mixture at 450°C. The solid lines correspond to a 15% $C_3^=$, 15% H_2 , 7.5% O_2 feed. The dashed line is the propylene conversion obtained with a 15% $C_3^=$, 0% H_2 , 7.5% O_2 feed. The selectivity of Bi_2O_3 for hydrogen combustion in the presence of propylene is still high,

although not as high as in the presence of propane. Furthermore, the propylene conversion is less when hydrogen is present.

EXAMPLE 8

- 5 A series of metal oxides were examined with the experiment described in Examples 2 and 3 to evaluate their SHC properties. These results of these experiments are summarized in the following table.

	<u>Metal Oxide</u>	<u>Flowrate, cc/min</u>	<u>H₂ Conv. %</u>	<u>C₃ = Conv., %</u>
10	Silica	170	10	<0.5
		40	<10	1.5
	Sb ₂ O ₃ /SiO ₂	170	40	<0.5
		40	16	1.5
15	Bi ₂ O ₃ /SiO ₂	170	>90	<0.5
		40	80	1.2
	Bi ₉ PW ₁₂ O _x	170	55	1.5
		40	61	5.5
	TbO _x /SiO ₂	170	16	1.0
		40	23	4.0
20	PbO _x /SiO ₂	170	16	<0.5
		40	<10	2.5
	WO ₃ /SiO ₂	170	22	<0.5
		40	<10	3.8
	ZnO ₂ /SiO ₂	170	20	0.8
		40	40	1.5
25	GdO _x /SiO ₂	170	10	<0.5
		40	<10	1.5
	InO _x /SiO ₂	170	18	1.4
		40	25	2.5
30	GaO _x /SiO ₂	170	<10	6.0
		40	<10	8.4
	GeO _x /SiO ₂	170	<10	<0.5
		40	<10	<1.0

EXAMPLE 9

In this Example, it is illustrated that higher than equilibrium propylene yields from propane can be obtained by using physical mixtures of appropriate dehydrogenation catalysts with SHC metal oxides.

A physical mixture with equal weights of Pt-Sn-ZSM-5 (0.65 % Pt) and 42% Bi₂O₃/58% SiO₂ was prepared by combining pelleted, 20-40 mesh size particles of the two materials. This mixture was compared to Pt-Sn-ZSM-5 for the dehydrogenation of propane to propylene at 540°C and 1 atm total pressure. A gas stream of pure propane was passed over 2 g of the mixed catalyst system at a flowrate of 17 cc/min for 166 sec. The reactor effluent was collected in an evacuated gas bulb and was analyzed. The same experiment was also conducted with 1 g Pt-Sn-ZSM-5. The product analysis in each case was as follows, wherein C₃ stands for propane, C₃⁼ stands for propylene, CO_x stands for CO + CO₂ and C₃⁻ stands for cracked products.

	<u>Catalyst</u>	<u>C₃ Conv.</u>	<u>C₃⁼ Yield</u>	<u>CO_x Yield</u>	<u>C₃⁻ Yield</u>
20	Pt-Sn-ZSM-5	24.2	22.1	0.6	1.5
	Mixture	47.0	42.0	3.0	2.0

EXAMPLE 10

The same experiment as in Example 9 was conducted over the mixed catalyst system, except that feed was passed over the catalyst for 332 sec. Propane conversion was 42.8%, and propylene, CO_x and cracked product yields were 38.8, 1.9, and 2.0%, respectively.

EXAMPLE 11

The same experiment as in Example 9 was conducted over the mixed catalyst system, except that feed was passed over the catalyst at a flowrate of 8.5 cc/ min for 332 sec. Propane conversion was 47.8% and propylene, CO_x, and

cracked product yields were 39.7, 4.7, and 3.4%, respectively.

EXAMPLE 12

5 The same experiment as in Example 9 was conducted over a mixture of 2 g Pt-Sn-ZSM-5 and 1 g $\text{Bi}_2\text{O}_3/\text{SiO}_2$. Propane conversion in the collected product was 50.2% and propylene, CO_x , and cracked product yields were 40.7, 4.6, and 4.9%, respectively.

EXAMPLE 13

10 1g of Pt/Sn/ZSM-5 was mixed with 1g of the metal oxide to be tested. The catalyst mixture was first calcined in air at 500°C and the feed was 100% propane. The feed was passed over the catalyst mixture at 17 cc/min (corresponding to $\text{WHSV}=2\text{g/gPt/Sn/ZSM-5}\cdot\text{hour}$) for 332
15 seconds. The reactor effluent was collected in an evacuated glass bulb and was analyzed. The propylene and CO_x yields obtained with each metal oxide are shown in Table 2 below. The base case experiment is with no metal oxide.

20 In Table 2, $\text{C}_3^{\text{= sel.}}$ stands for $\text{C}_3^{\text{= Yield}}$ divided by C_3 Conversion.

Table 2

	<u>Catalyst</u>	<u>C₃ = Yld</u>	<u>CO_x Yld</u>	<u>C₃ Conv.</u>	<u>C₃ = Sel.</u>
	Bi ₂ O ₃ /SiO ₂	.308	.017	.325	.948
	BiLaO _x /SiO ₂	.301	.022	.323	.932
5	BiSbO _x /SiO ₂	.260	.010	.270	.963
	Bi ₂ MO ₃ O ₁₂ /SiO ₂	.207	.074	.281	.737
	In ₂ MO ₃ O ₁₂ /SiO ₂	.334	.020	.354	.944
	In ₂ MoO ₆ /SiO ₂	.237	.009	.246	.963
10	No Met. Oxide	.183	.020	.203	.901
	Al ₂ MO ₃ O ₁₂ /SiO ₂ /SiO ₂	.179	.039	.218	.821
	Cr ₂ MO ₃ O ₁₂ /SiO ₂	.181	.046	.227	.797
	MoO ₃ /SiO ₂	.160	.038	.198	.808
15	Fe ₂ O ₃ /SiO ₂	.188	.051	.239	.787
	Nb ₂ O ₅ /SiO ₂	.188	.031	.219	.858
	V ₂ O ₅ /SiO ₂	.164	.147	.311	.527

Claims:

1. A process for converting an alkane of the formula,
$$\text{C}_n\text{H}_{2n+2},$$

to an alkene of the formula,
$$\text{C}_n\text{H}_{2n},$$

5 where n is the same for the alkane and the alkene and n is from 2 to 5, the process comprising the steps of:
(a) contacting the alkane with a solid material comprising a dehydrogenation catalyst under conditions sufficient to produce the alkene and
10 H_2 ;
(b) contacting the effluent from step (a) with an oxidation catalyst and oxygen under conditions sufficient to selectively convert the H_2 to
15 water; and
(c) contacting at least a portion of the effluent of step (b) with a solid material comprising a dehydrogenation catalyst under conditions sufficient to convert unreacted alkane to
20 additional quantities of the alkane and H_2 .
2. The process of claim 1 wherein the dehydrogenation catalyst comprises at least one metal selected from Cr, Mo, Ga, Zn and a Group VIII metal and the oxidation catalyst comprises an oxide of at least one
25 metal selected from Bi, In, Sb, Zn, Tl, Pb and Te.
3. The process according to claim 1, wherein step (c) is accomplished by recycling effluent from the reaction zone of step (b) to the reaction zone of step (a).
4. The process according to claim 1, wherein step (c) is
30 conducted in a reaction zone separate from the reaction zone of step (a).

5. The process according to claim 4, wherein the entire effluent from step (b) is used in step (c).
6. The process according to claim 1, wherein the alkane is ethane or propane.
- 5 7. The process according to claim 1, wherein the alkane is isobutane and/or n-butane.
8. The process according to claim 1, wherein the dehydrogenation catalyst comprises platinum.
9. The process according to claim 1, wherein the
10 oxidation catalyst comprises an oxide of indium or Bi_2O_3 .
10. The process according to claim 1, wherein the metal oxide catalyst comprises a mixed metal oxide containing bismuth.
- 15 11. The process according to claim 1, wherein the oxidation catalyst comprises Sb_2O_4 or a mixed metal oxide containing antimony.
12. The process according to claim 1, wherein the
20 oxidation catalyst comprises $\text{Bi}_a\text{Sb}_b\text{O}_x$, where a and b are each greater than 0 and less than or equal to 12 and x is determined by the oxidation states of Bi and Sb under reaction conditions.
13. The process according to claim 5, wherein the
25 dehydrogenation catalyst comprises platinum and the oxidation catalyst contains bismuth, antimony, indium, or molybdenum, or a mixture thereof.

14. The process according to claim 1, wherein the oxidation catalyst comprises one or more oxides of an element selected from Mo, W, P and La.
- 5 15. The process according to claim 1 wherein the dehydrogenation catalyst comprises 0.1 to 20 weight percent platinum and 0.1 to 20 weight percent tin, with the remainder of the dehydrogenation catalyst being ZSM-5.

FIG. 1

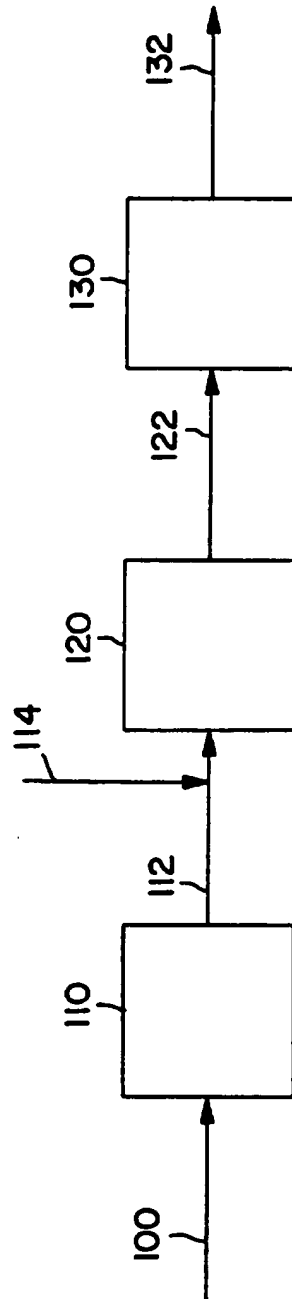
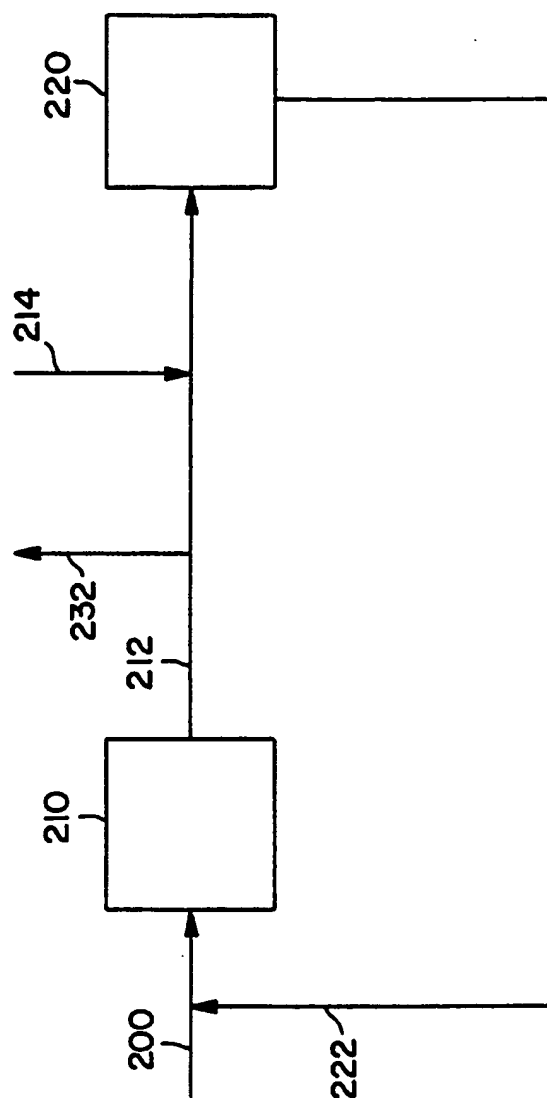
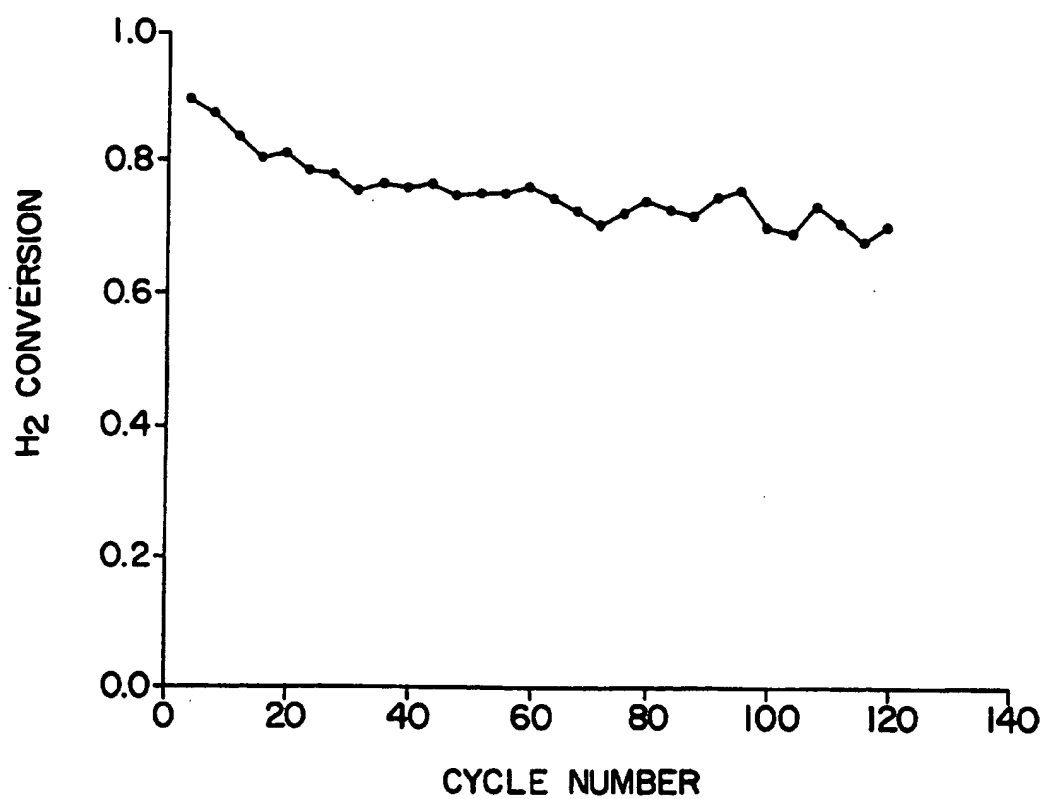


FIG. 2



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FIG. 3



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FIG. 4

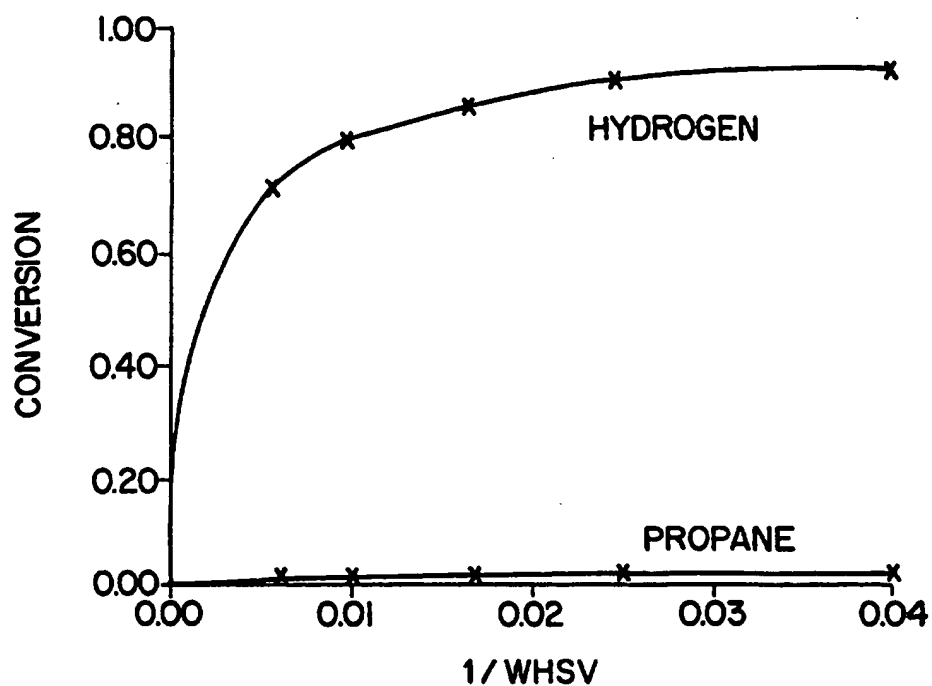
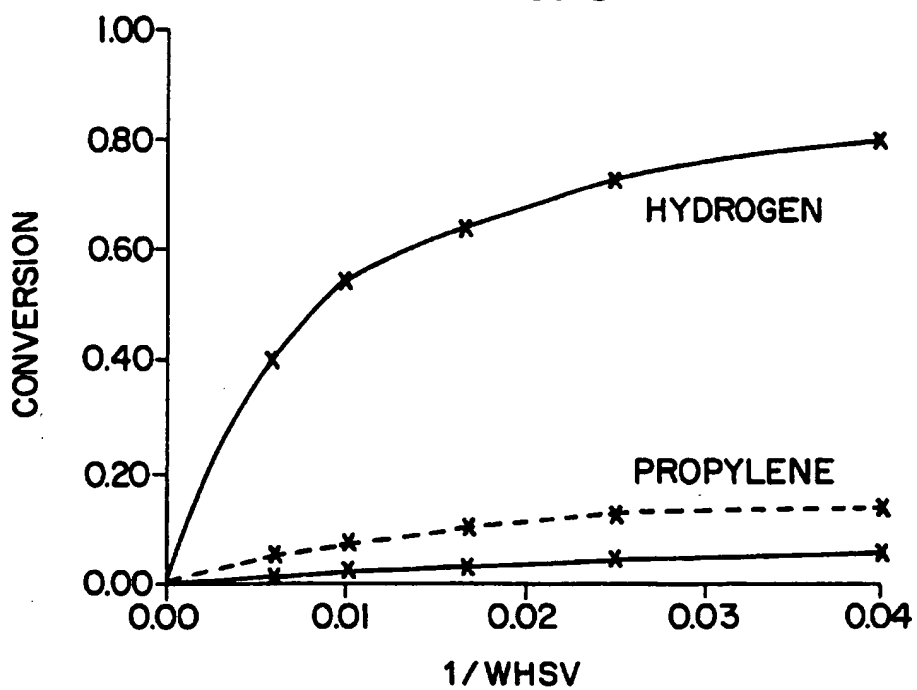


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/05975

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07C 5/333

US CL : 585/621, 626, 629, 630, 631, 656, 658, 659, 660, 662, 663

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/621, 626, 629, 630, 631, 656, 658, 659, 660, 662, 663

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,250,346 (YOUNG ET AL.) 10 February 1981, abstract, summary of invention	1-15
Y	US, A, 4,568,790 (MCCAIN) 04 February 1986, abstract, columns 2-4	1-15
Y	US, A, 4,778,941 (TAGAMOLILA) 18 October 1988, Figure 1 and associated descriptions	1-15
Y	US, A, 4,806,624 (HERBER ET AL.) 21 February 1989, Figure and associated descriptions.	1-15

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	* T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

13 JULY 1995

Date of mailing of the international search report

10 AUG 1995

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